Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Fluoride-Triggered Indium-Mediated Synthesis of (Hetero)biaryls

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General methods. All ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz instrument in $CDCl_3$, unless otherwise stated. All reactions were carried out in dried glassware. Tetrahydrofuran (THF) was dried by distillation from sodium and benzophenone. 3-Iodopyridine, iodobenzene, 2-iodothiophene, 4-bromobenzaldehyde, 4-iodoacetophenone, triethoxyphenylsilane, 2-(triethoxysilyl)thiophene, tetrabutylammonium fluoride (TBAF), *N*,*N*-diisopropylethylamine, indium (III) choride, 1-methyl-2-pyrrolidinone (NMP), tetrakis(triphenylphosphine) palladium (0) and [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II) complex with dichloromethane are commercially available and were used as received. 4-(Triethoxysilyl)acetophenone was prepared according to described procedures.[1]

(1) A. S. Manoso and P. DeShong, *J. Org. Chem.*, 2001, **66**, 7449-7455.

Synthesis of 3-(triethoxysilyl)pyridine (3).[1] 3-iodopyridine (1.025 g, 5 mmol) and *i*-Pr_2NEt (2.6 mL, 15 mmol) were added to a stirring solution of $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (122 mg, 0.15 mmol) in 20 mL of NMP under an atmosphere of argon. Triethoxysilane (1.385 mL, 7.5 mmol) was added. The reaction was heated at 80 °C (12 h). After cooling at room temperature, the reaction mixture was extracted with pentane (3 x 25 mL). The combined extracts were washed with water to remove NMP, dried over $MgSO_4$, filtered, and concentrated. The resulting oil was purified by distillation (125 °C, 0.5 mmHg) to give 651 mg (54% yield) of a colorless oil.

^{1}H NMR δ 1.17 (t, 9 H, *J* = 6.9 Hz), 3.81 (q, 6 H, *J* = 6.9 Hz), 7.18-7.24 (m, 1 H), 7.86 (d, 1 H, *J* = 6.0 Hz), 8.56 (d, 1 H, *J* = 6.0 Hz), 8.75 (s, 1 H); ^{13}C NMR δ 18.0, 58.7, 123.1, 126.5, 142.3, 151.0, 154.9

(1) M. Murata, K. Suzuki, S. Watanabe and Y. Masuda, *J. Org. Chem.*, 1997, **62**, 8569–8571.

^{1}H- and ^{13}C-NMR data of already known compounds

2-Phenylthiophene (1a).[1] ^{1}H NMR δ 7.05-7.08 (m, 1 H), 7.25-7.39 (m, 5 H), 7.59-7.62 (m, 2 H); ^{13}C NMR δ 123.0, 124.8, 125.9, 127.4, 127.9, 128.8, 134.4, 144.4

[2,2']-Bithienyl (2a).[1] ^{1}H NMR δ 7.15-7.20 (m, 4 H), 7.98-7.01 (m, 2 H); ^{13}C NMR δ 123.7, 124.3, 127.7, 137.4

3-(2-Thienyl)pyridine (3a).[1] ^{1}H NMR δ 7.10-7.37 (m, 4 H), 7.85-7.89 (m, 1 H), 8.56 (d, 1 H, *J* = 6.0 Hz), 8.89 (s, 1 H); ^{13}C NMR δ 123.4, 123.9, 125.8, 128.0, 130.2, 132.8, 140.0, 146.7, 148.1

***p*-Phenylbenzaldehyde (1b).** ^{1}H NMR δ 7.44-7.48 (m, 3 H), 7.61-7.65 (m, 2 H), 7.73 (d, 2 H, *J* = 9.0 Hz), 7.94 (d, 2 H, *J* = 9.0 Hz), 10.05 (s, 1 H); ^{13}C NMR δ 127.2, 127.5, 128.3, 128.9, 130.1, 135.0, 139.5, 146.9, 191.7

***p*-Thienylacetophenone (2c).** ^{1}H NMR δ 2.60 (s, 1 H), 7.11 (dd, 1 H, J_1 = 5.1 Hz, J_2 = 3.6 Hz), 7.35 (d, 1 H, *J* = 5.1 Hz), 7.41 (d, 1 H, *J* = 3.6 Hz), 7.68 (d, 2 H, *J* = 8.3 Hz), 7.95 (d, 2 H, *J* = 8.3 Hz); ^{13}C NMR δ 26.5, 124.5, 125.6, 126.4, 128.3, 129.0, 135.7, 138.7, 142.9, 197.2

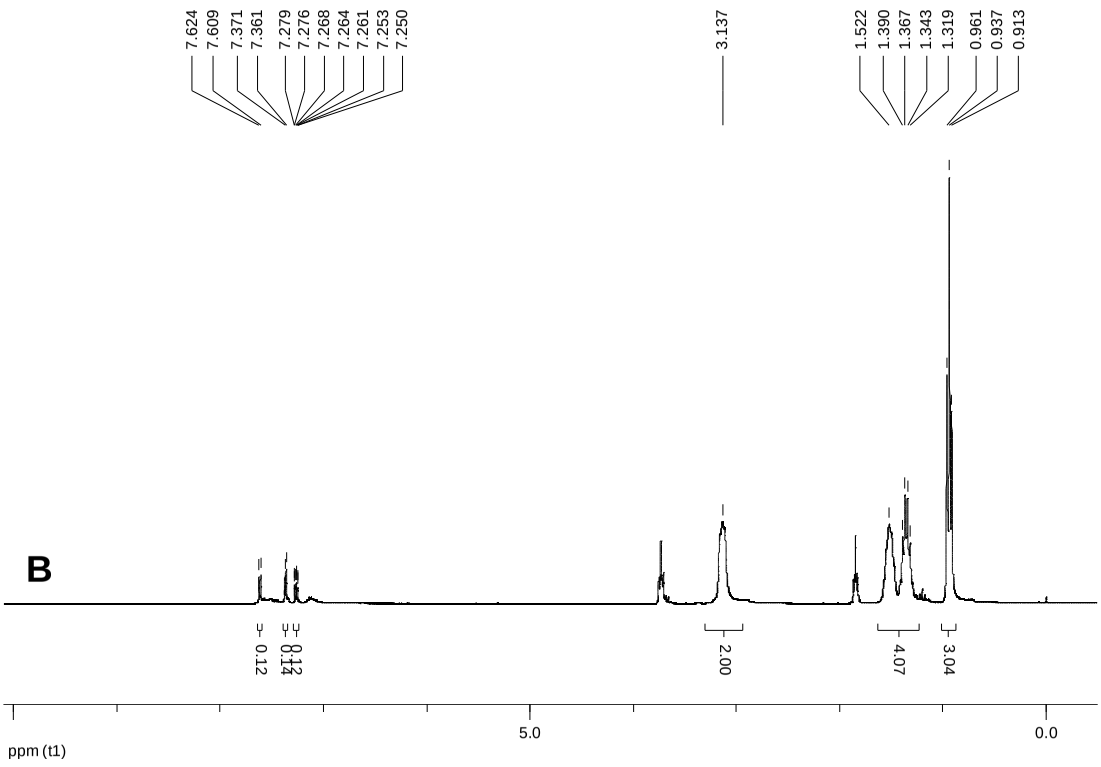
(1) E. Font-Sanchis, F. J. Céspedes-Guirao, A. Sastre-Santos and F. Fernández-Lázaro, *J. Org. Chem.*, 2007, **72**, 3589-3591.

Isolation and NMR characterization of the intermediate species

A solution of TBAF (1 M in THF, 1 mmol) was added to a stirring solution of $InCl_3$ (0.33 mmol) and 2-(triethoxysilyl)thiophene (1 mmol) in THF (20 mL). After 1 hour at room temperature, the solution was concentrated and ^{1}H-NMR spectrum in $CDCl_3$ (spectrum B, pages **S6**, **S7** and **S8**) or ^{13}C-NMR spectrum in THF-d_8 (spectrum B, pages **S9**, **S10** and **S11**) was performed to the residue.

A solution of thienyllithium (1 M in THF, 1 mmol) was added to a stirring solution of $InCl_3$ (0.33 mmol) in THF (20 mL). After 1 hour at room temperature, the solution was concentrated and ^{1}H-NMR spectrum in $CDCl_3$ (spectrum C, pages **S7** and **S8**) or ^{13}C-NMR spectrum in THF-d_8 (spectrum C, pages **S10** and **S11**) was performed to the residue.

^{1}H-NMR spectrum in $CDCl_3$ (spectrum A, pages **S6** and **S8**) and ^{13}C-NMR spectrum in THF-d_8 (spectrum A, **S9** and **S11**) of commercially available 2-(triethoxysilyl)thiophene are also provided for comparison.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1.367
1.343
1.319
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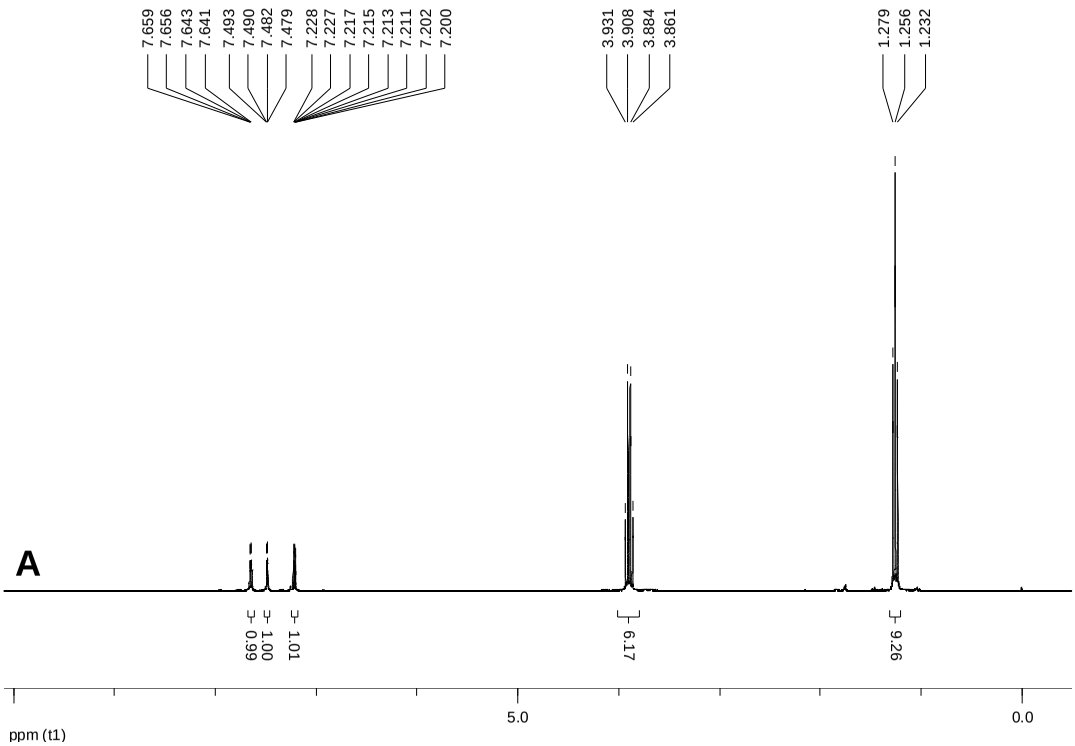
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7.202
7.200
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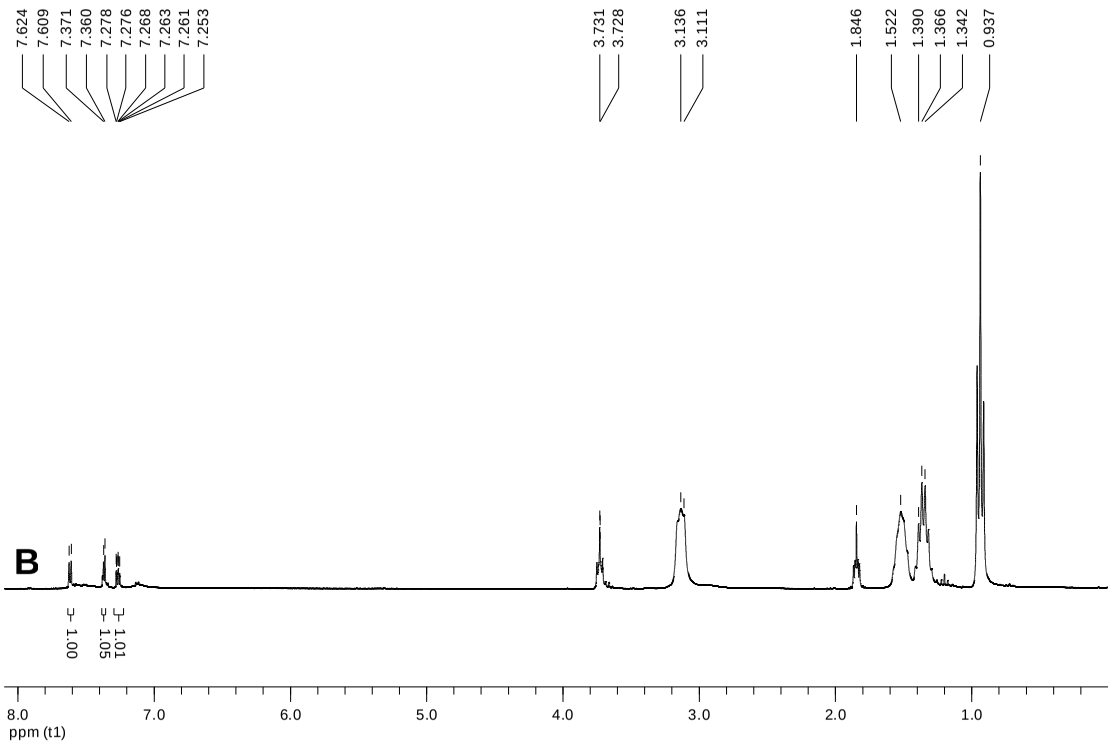
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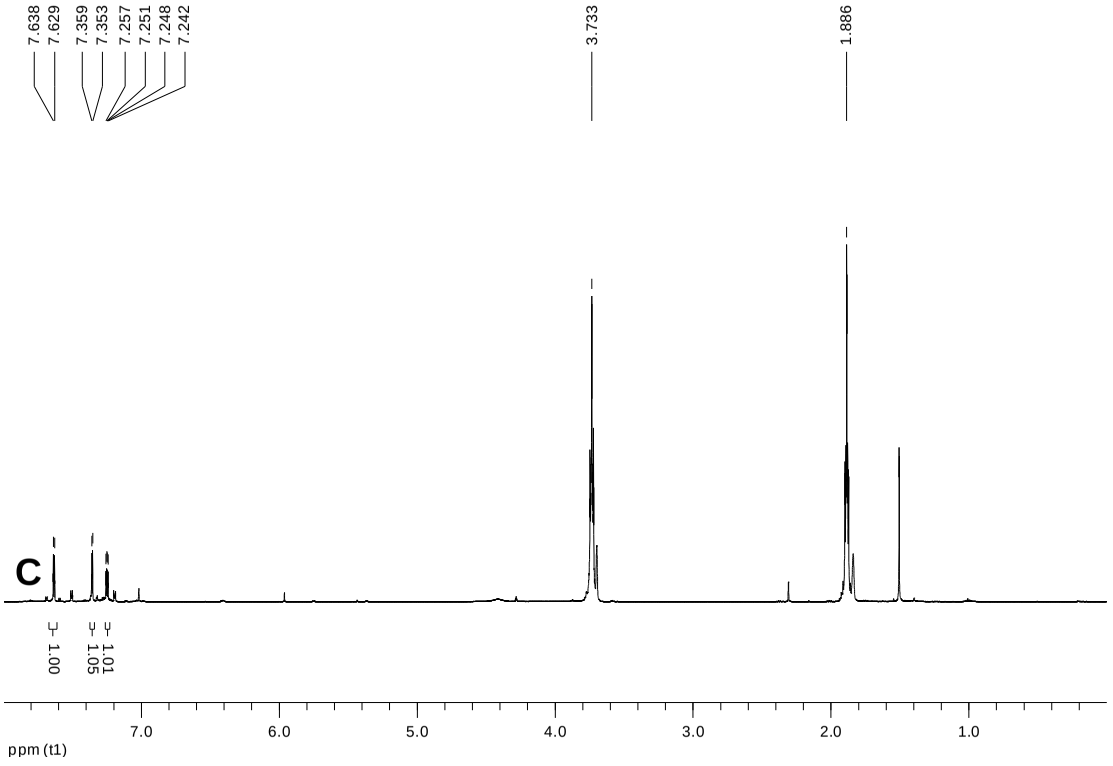
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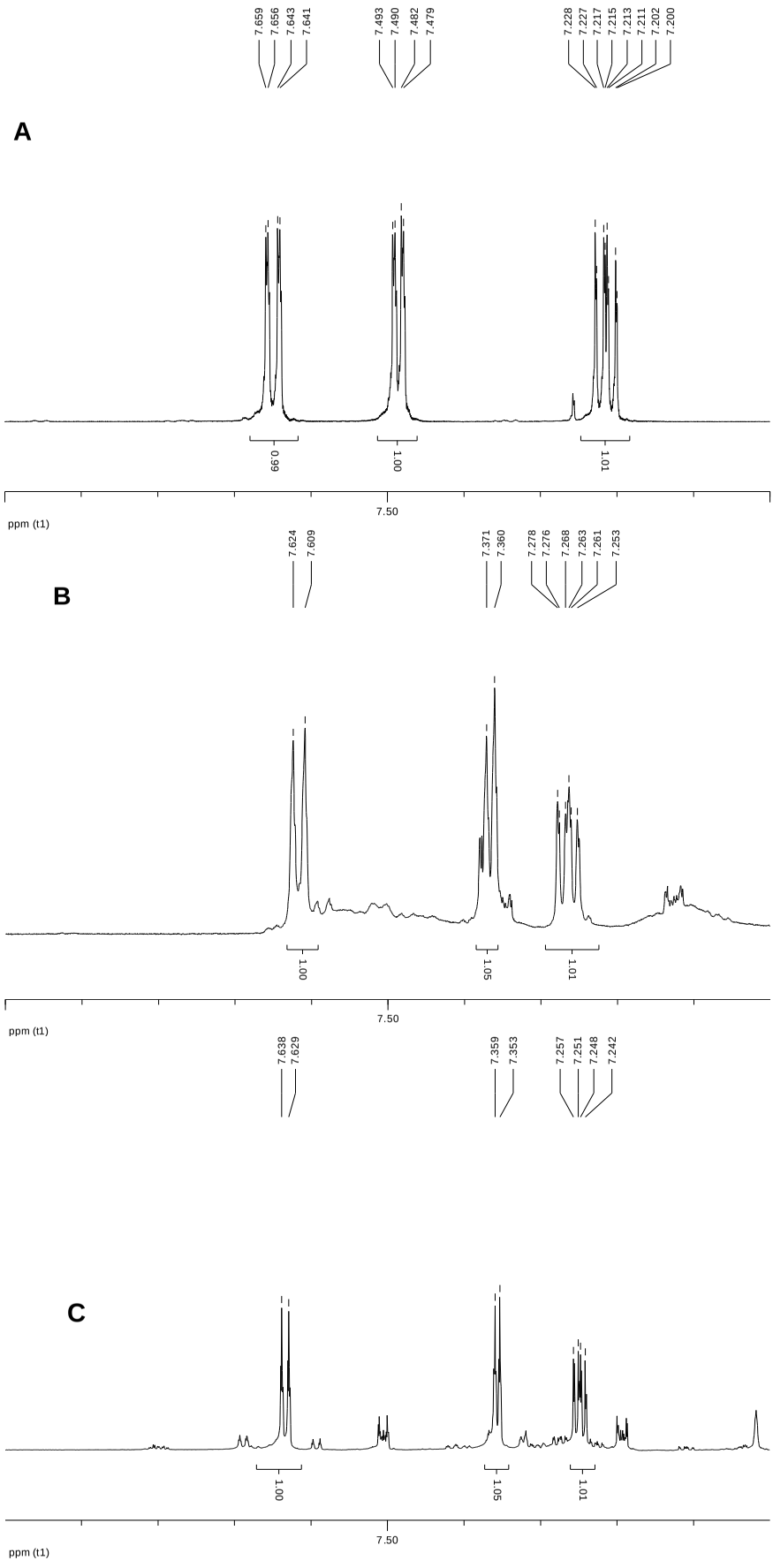
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ppm (t1)
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ppm (t1)
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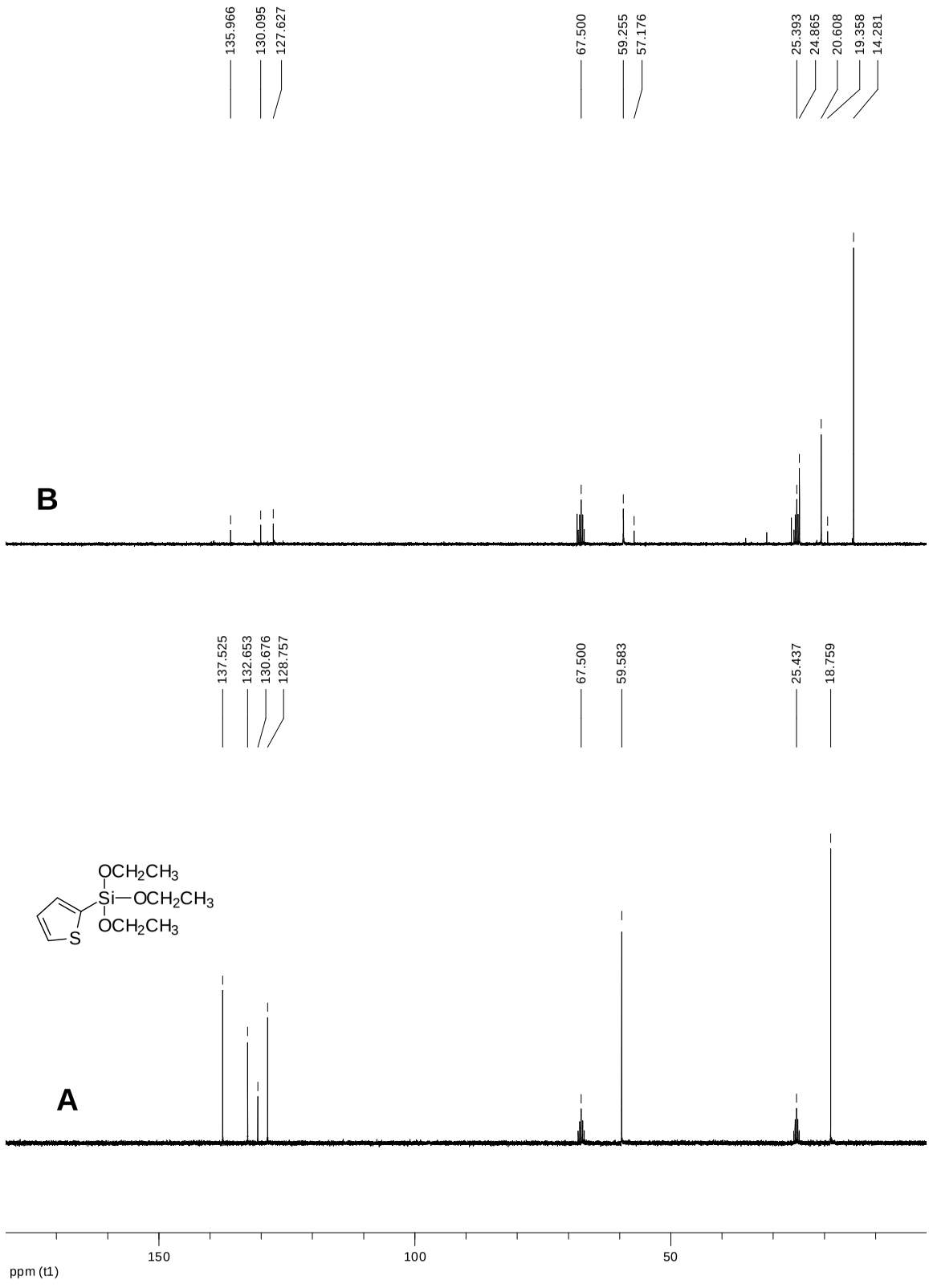
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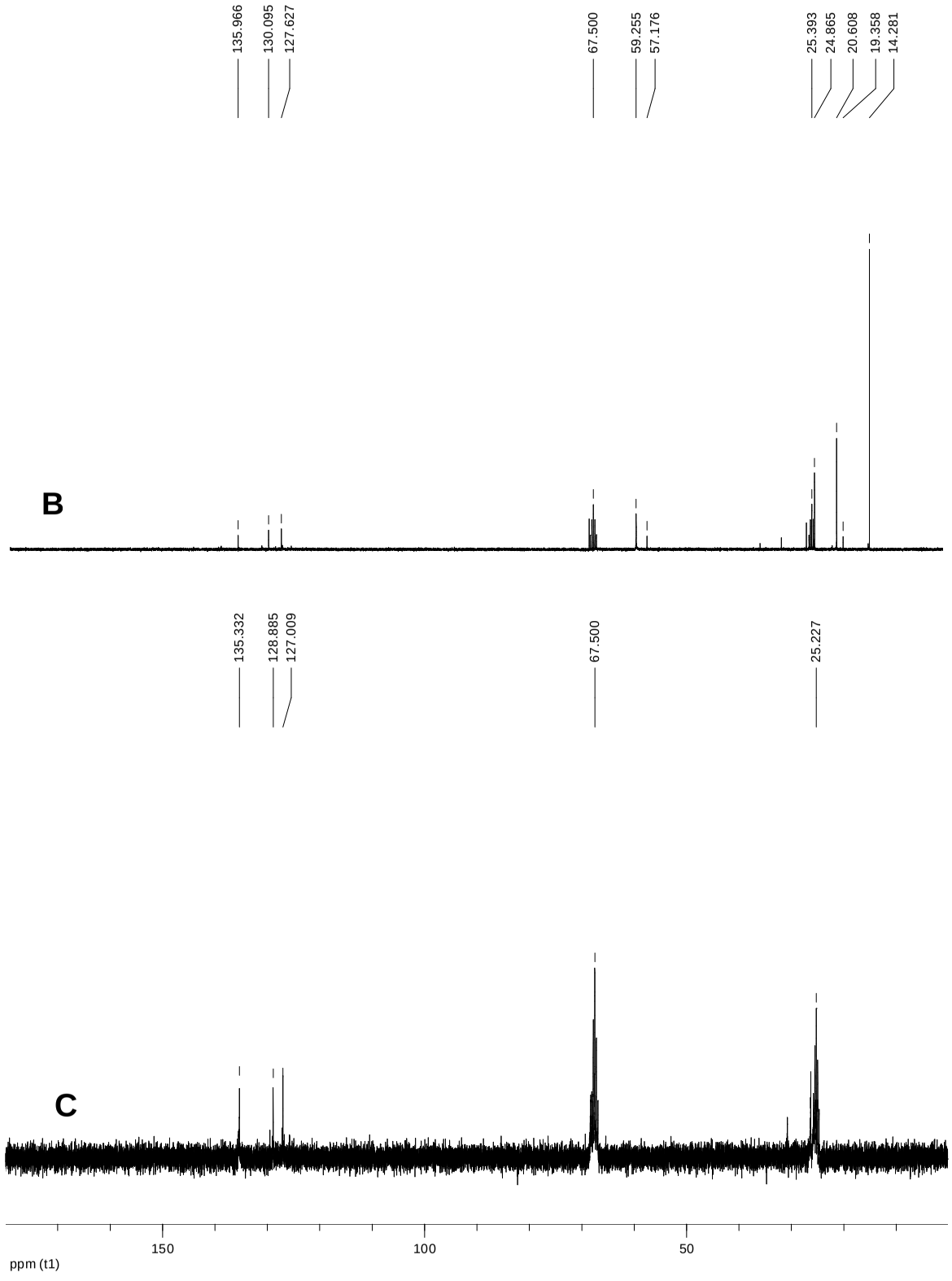
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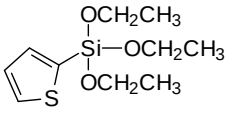
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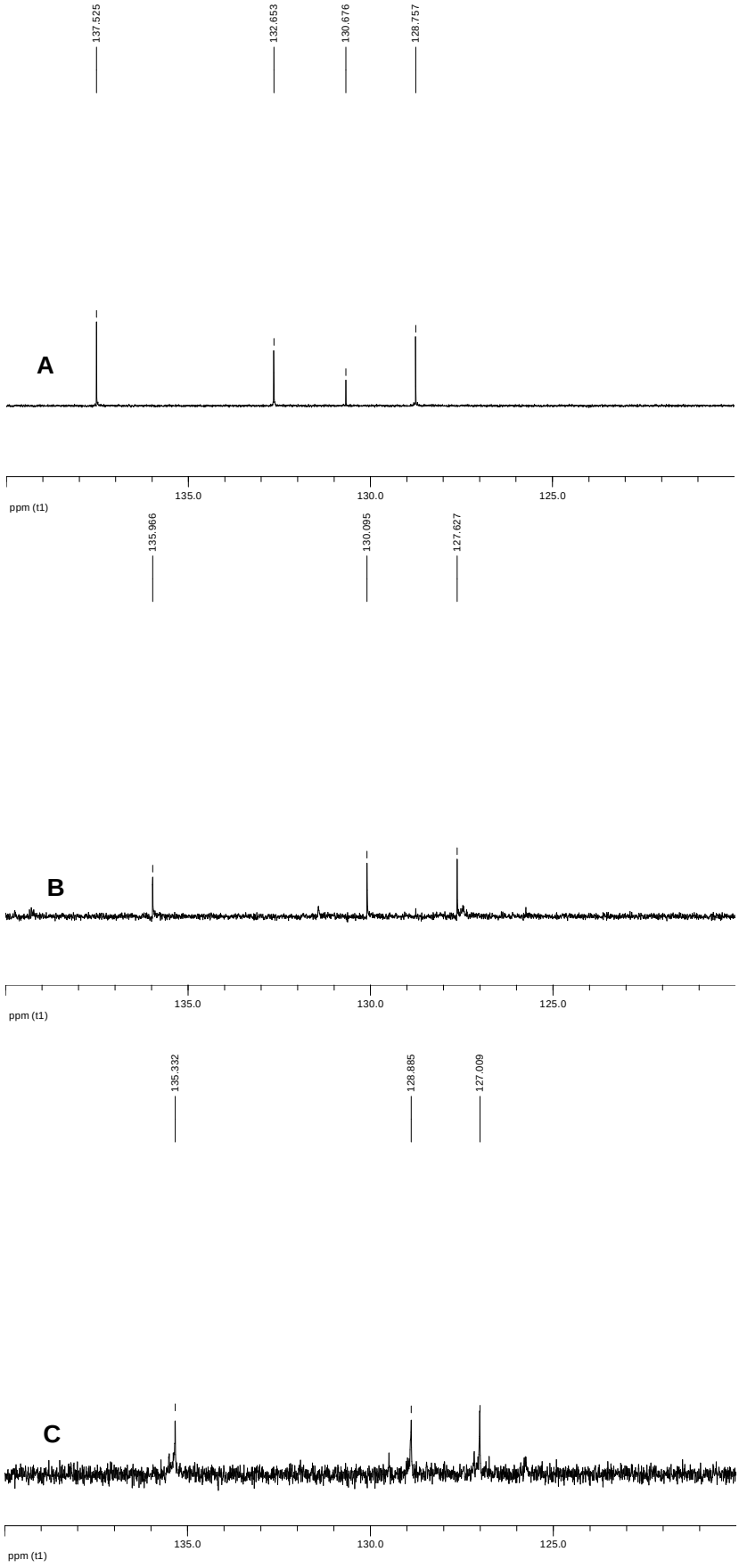
S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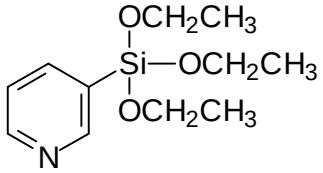
^{1}H- and ^{13}C-NMR spectra



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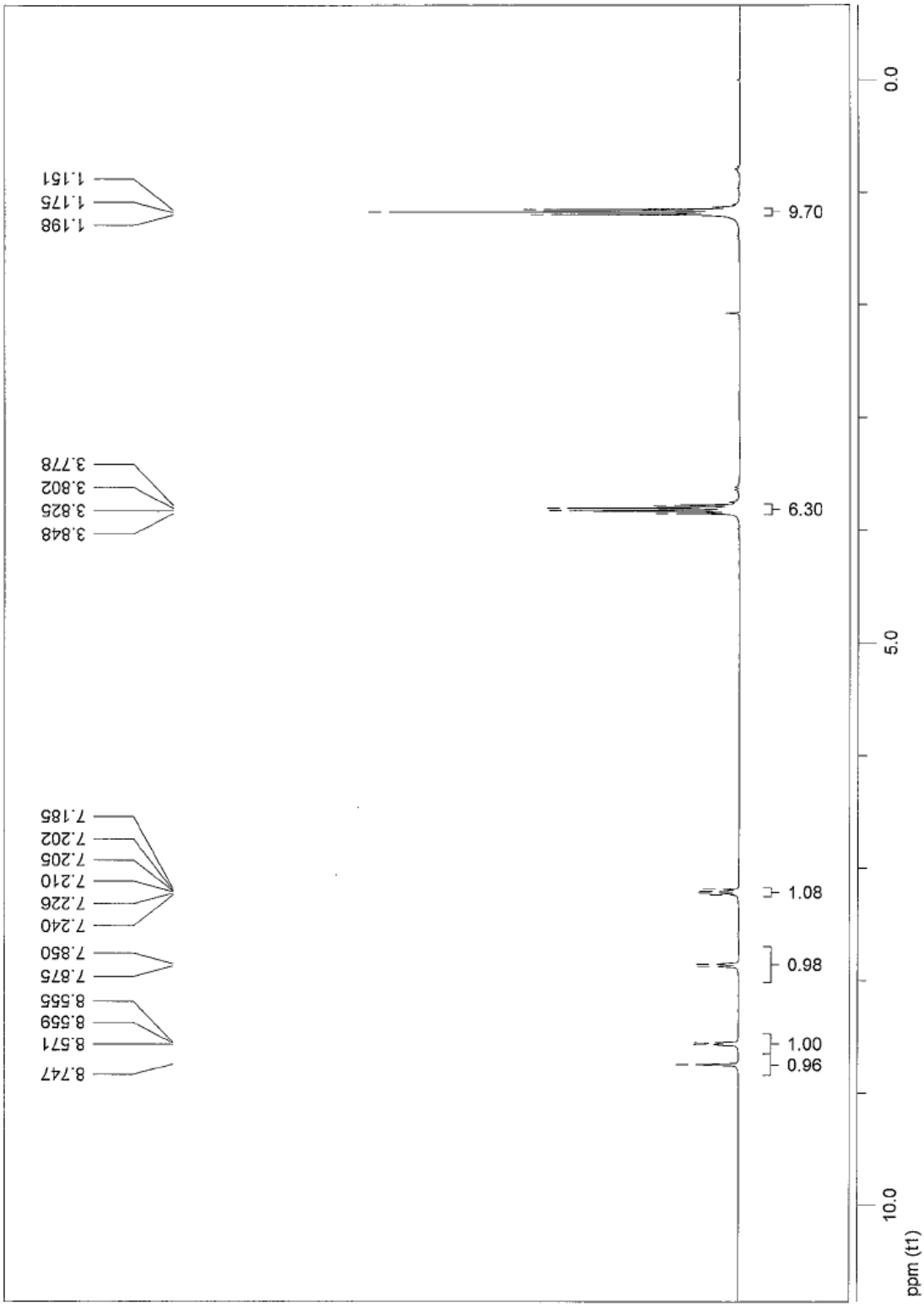

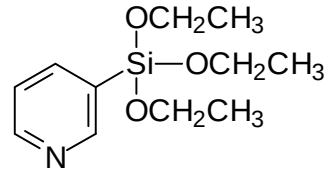
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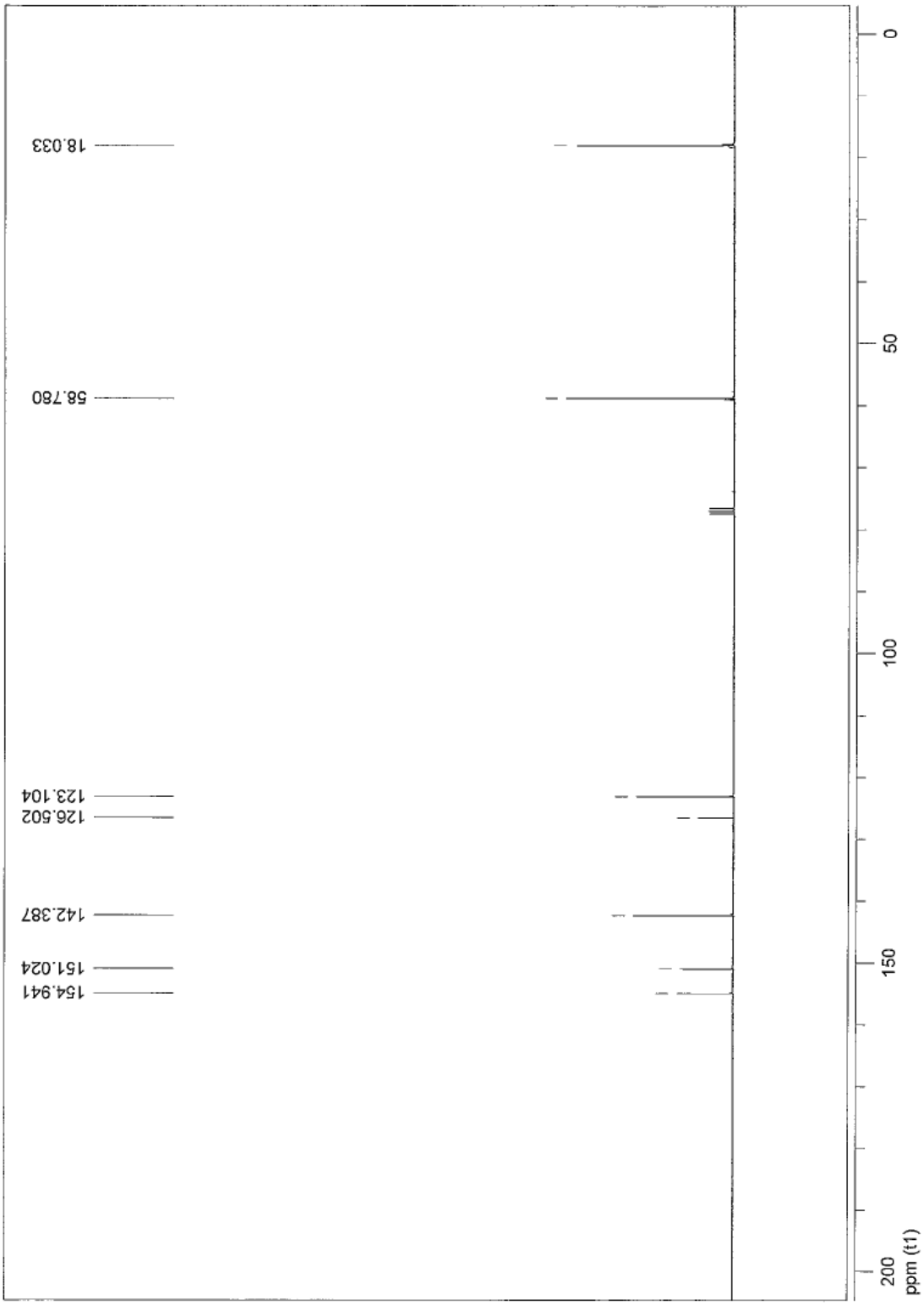
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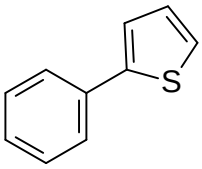
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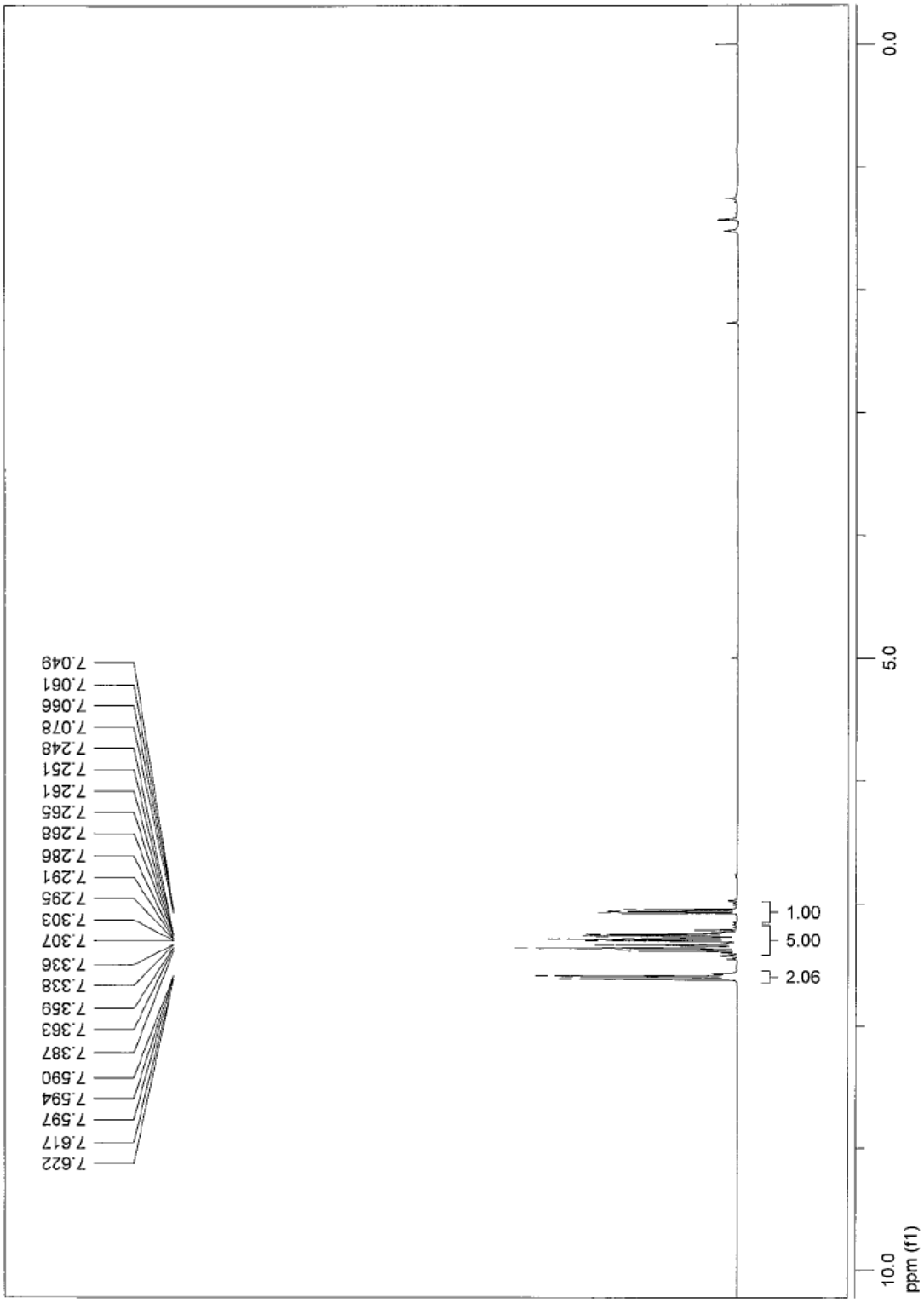
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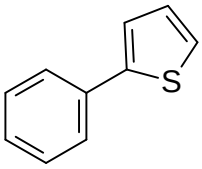
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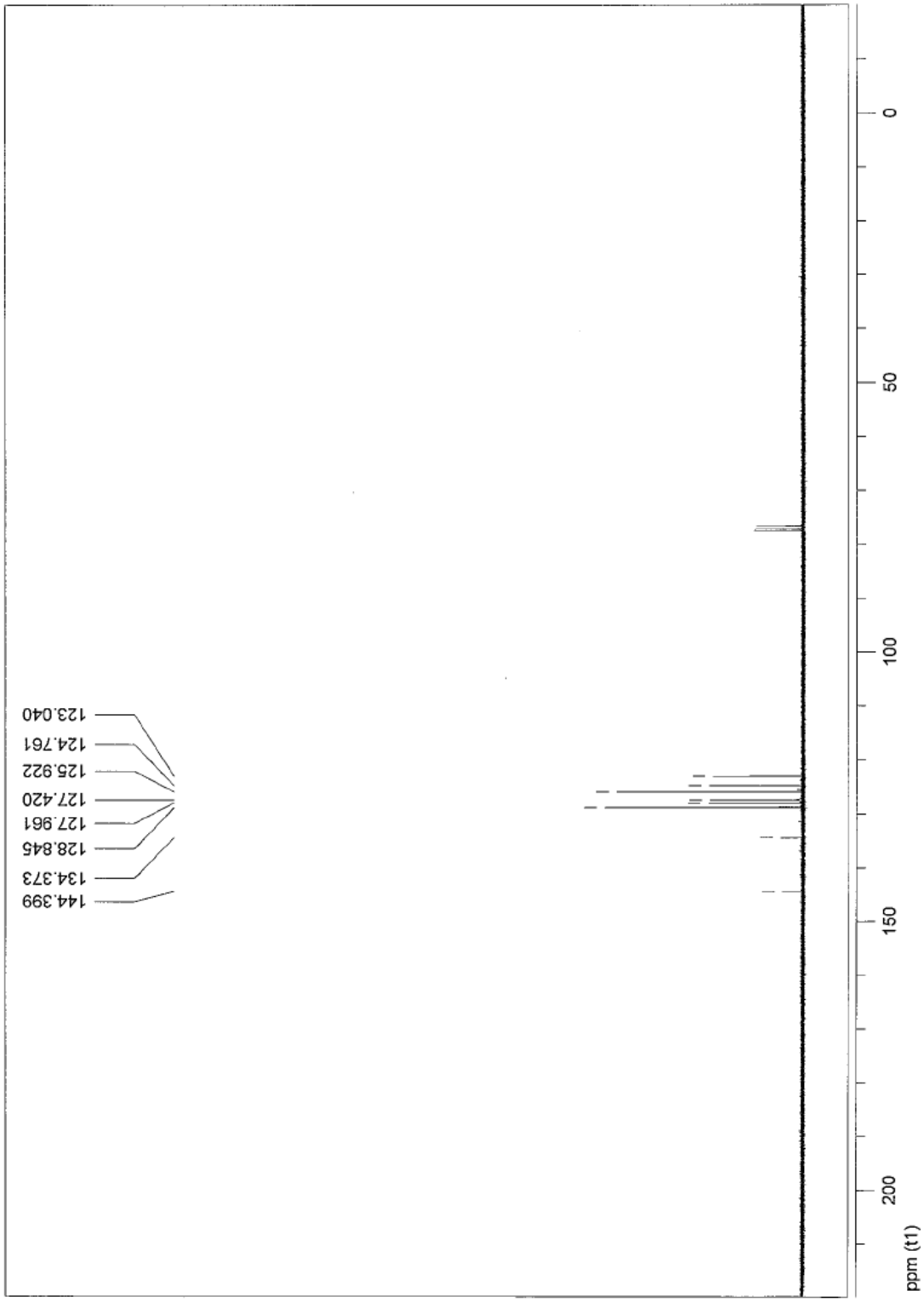
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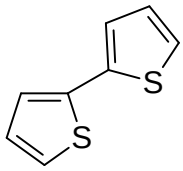
S
S

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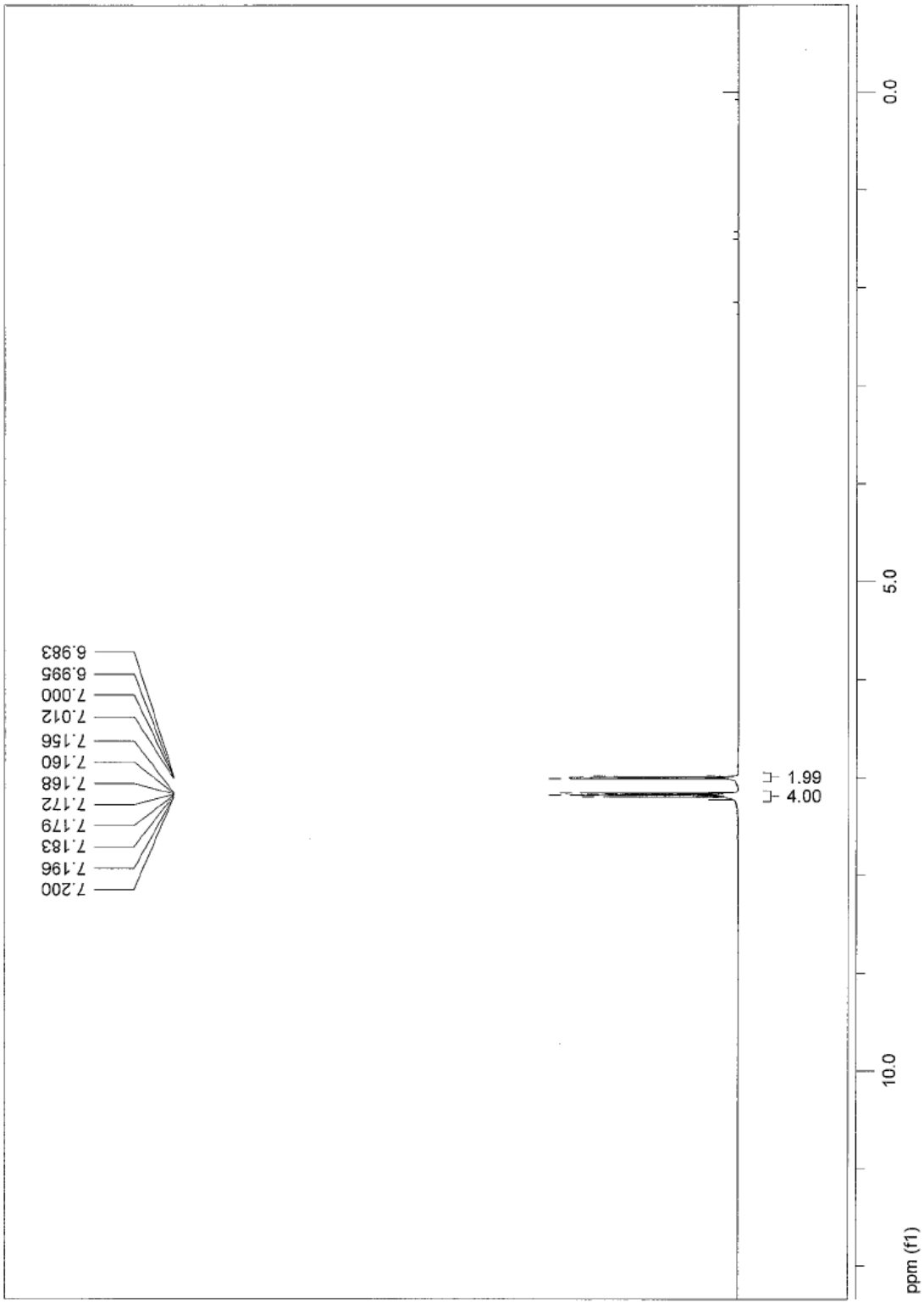
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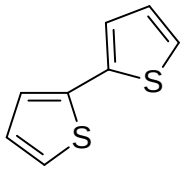

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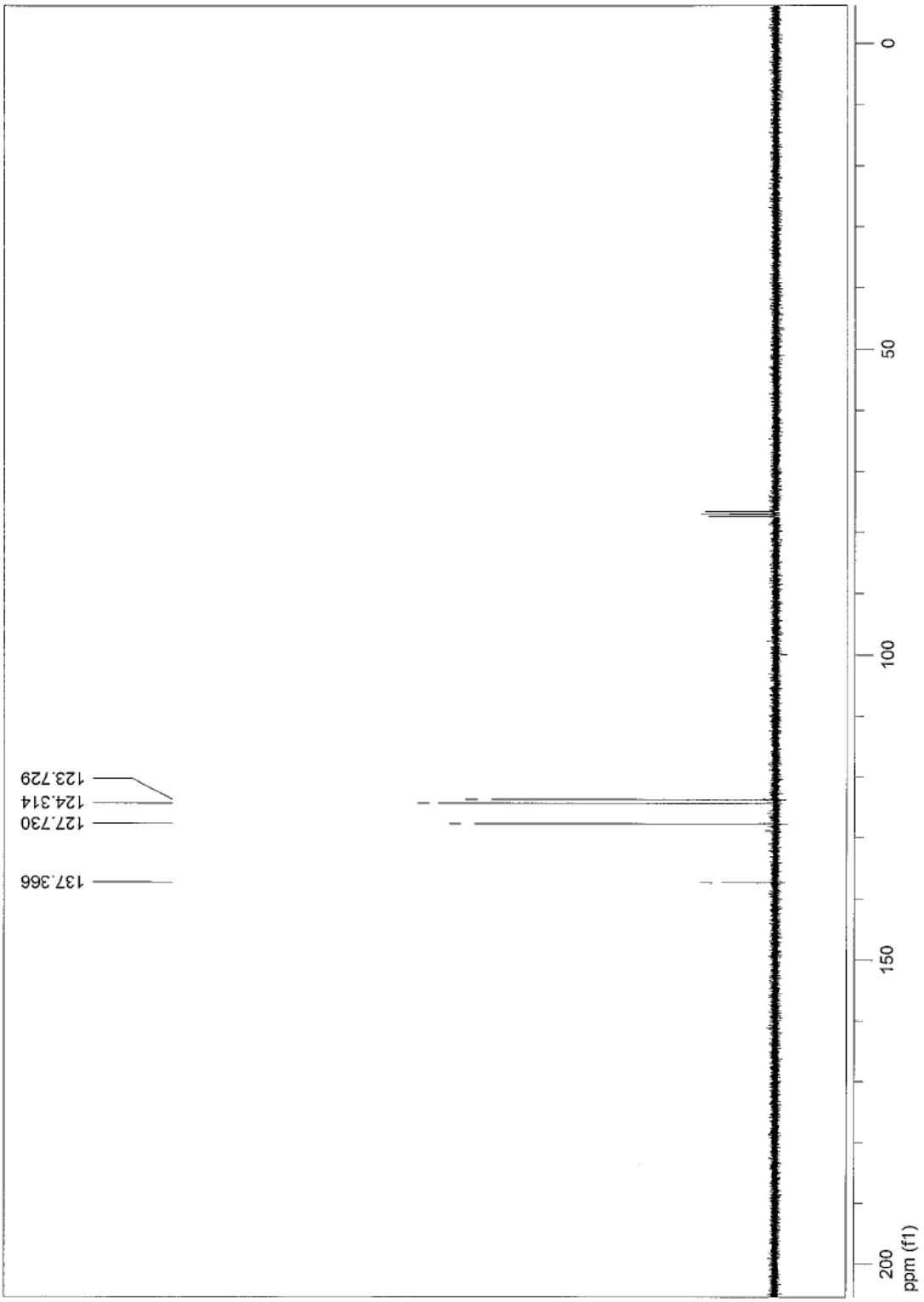


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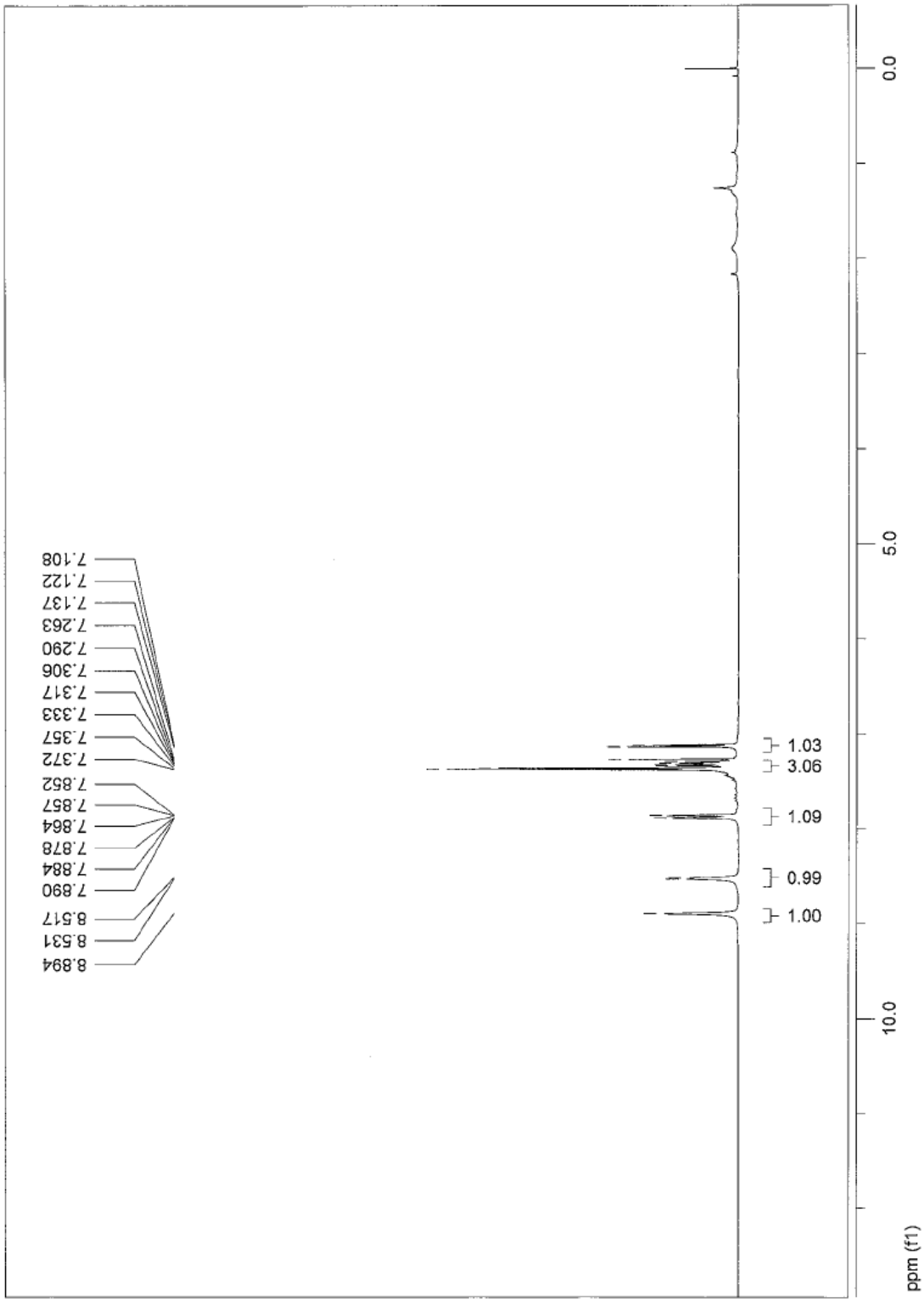
(3a)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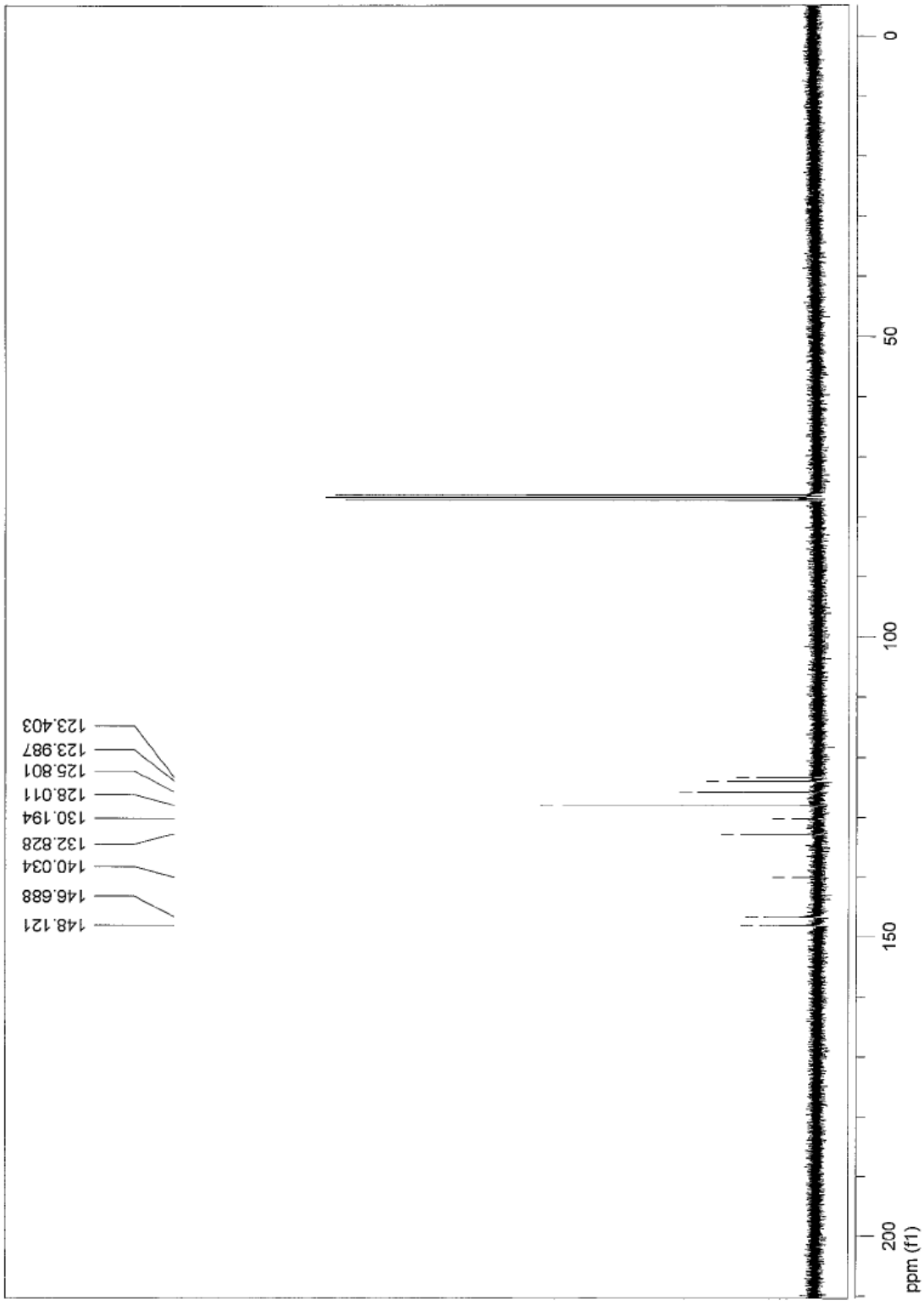
N

(3a)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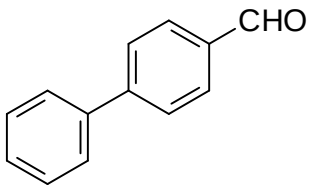
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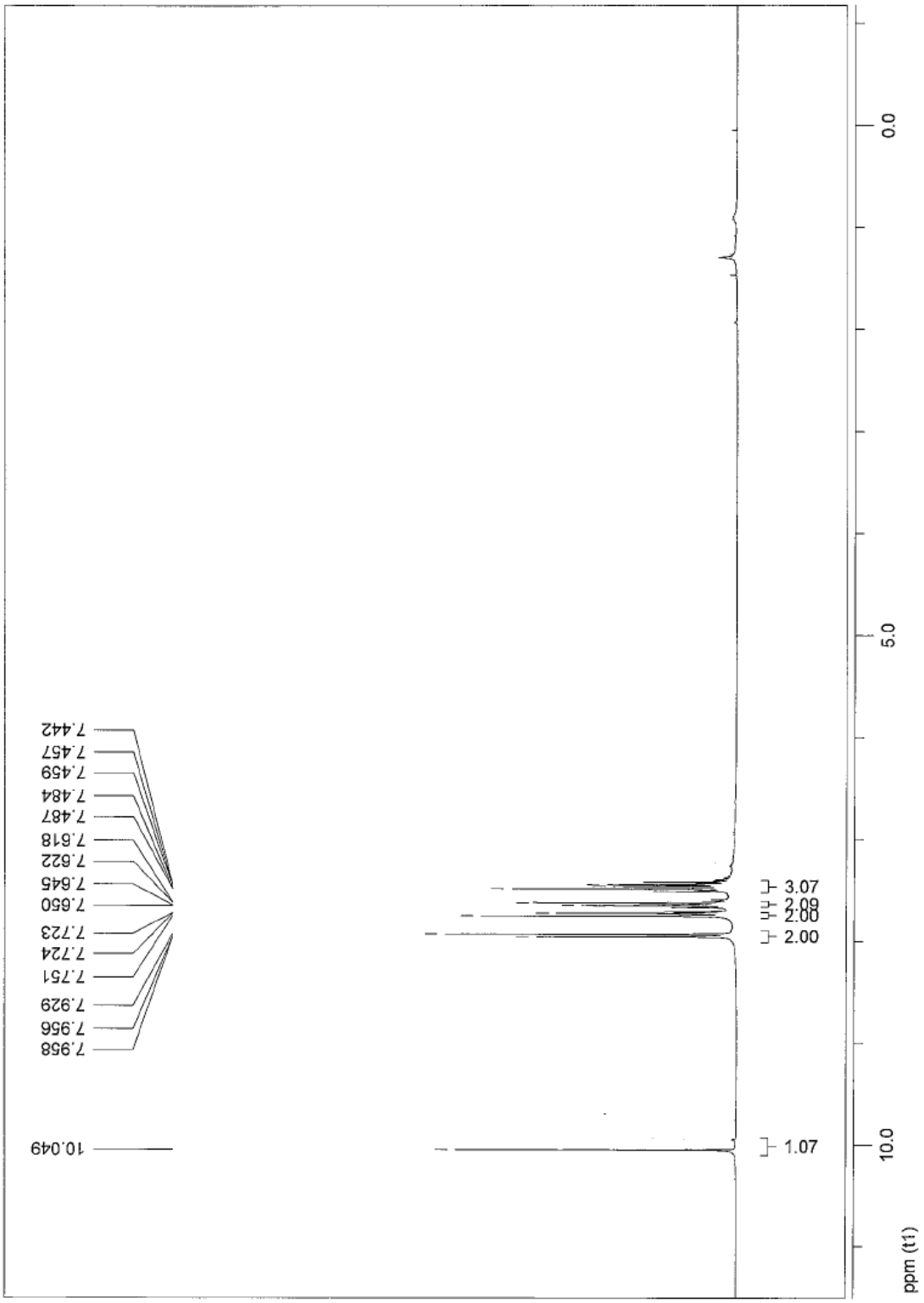
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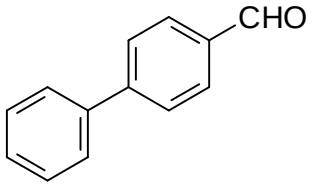
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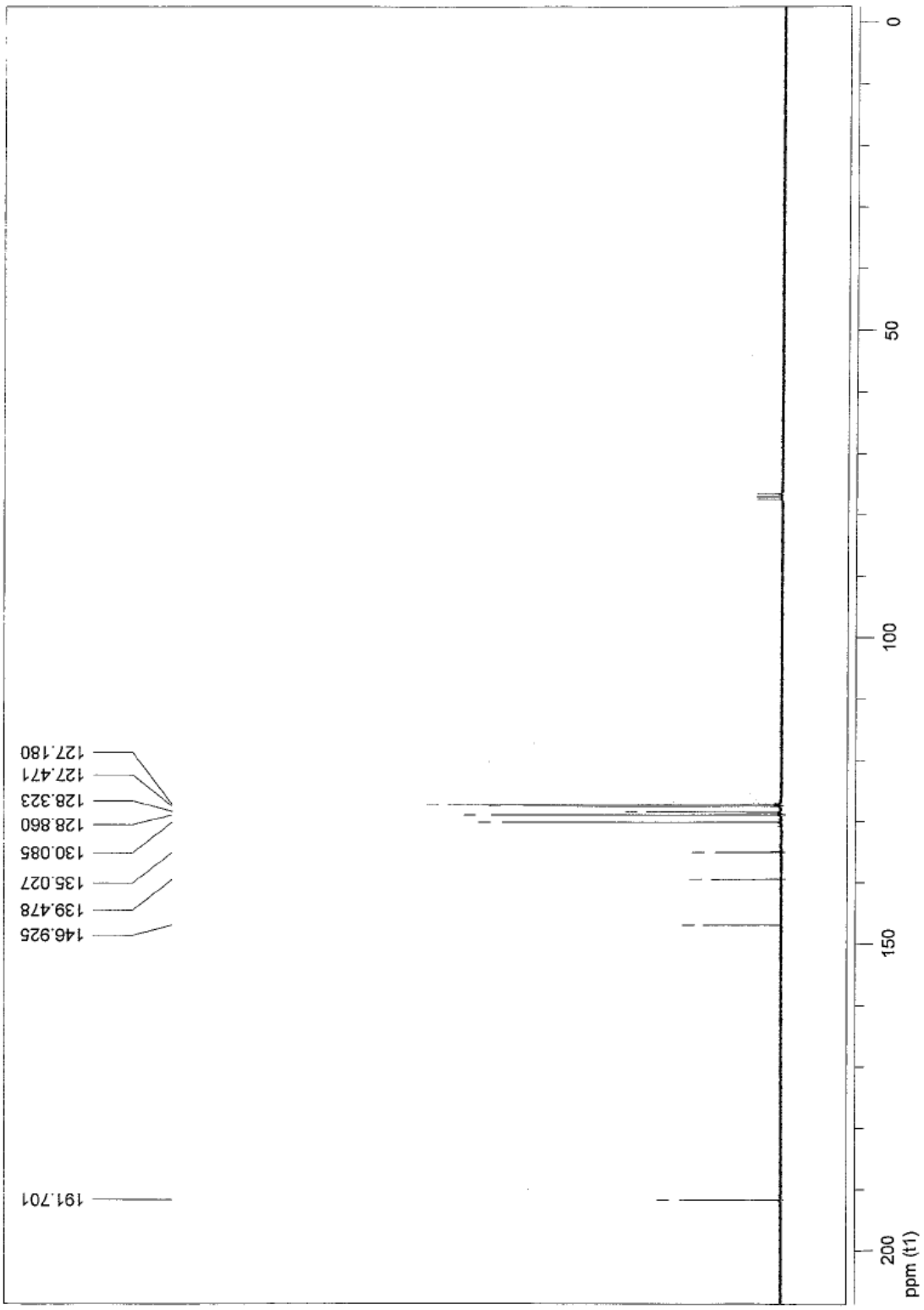
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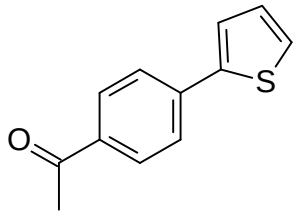
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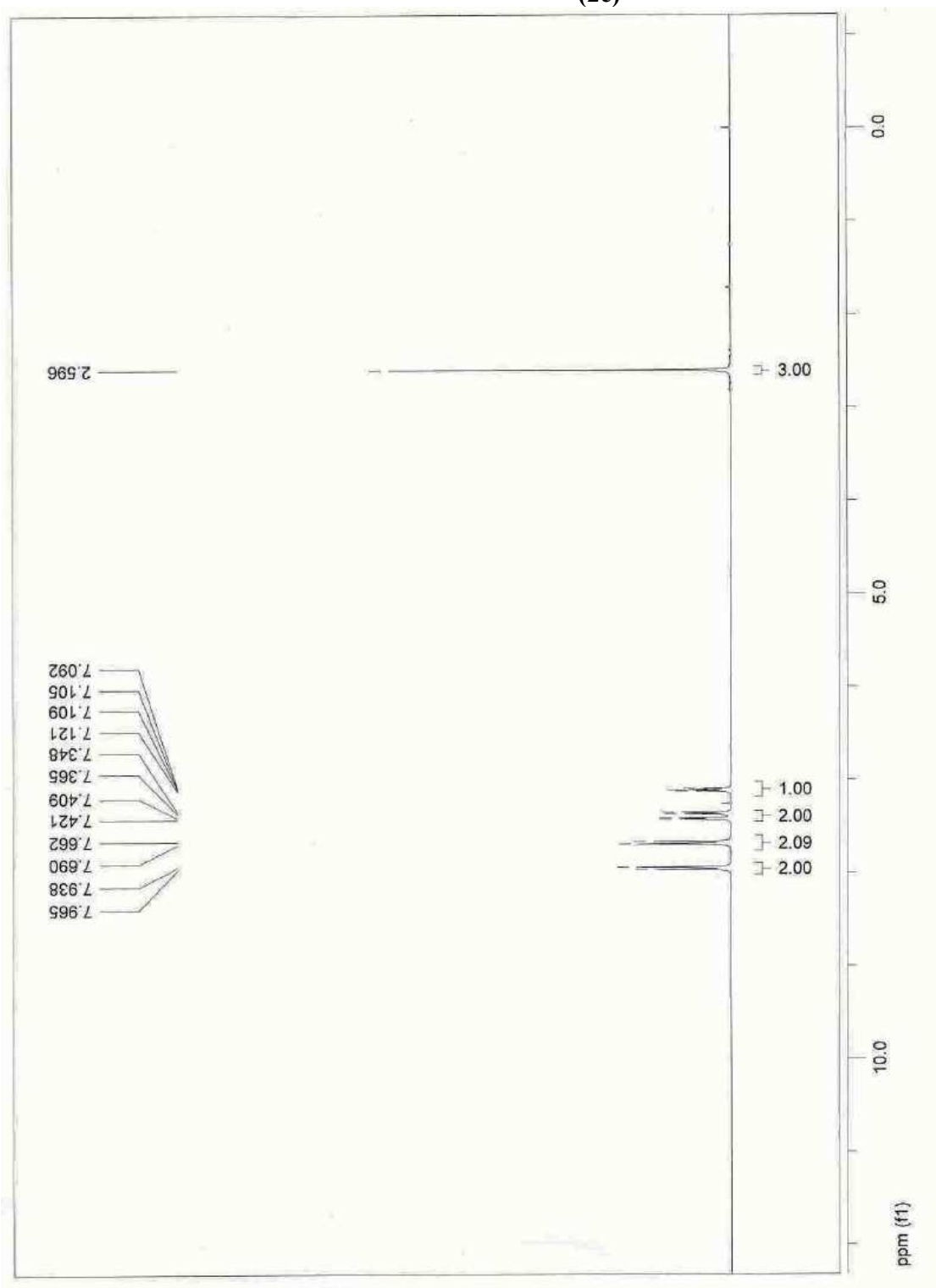
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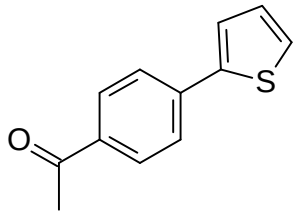
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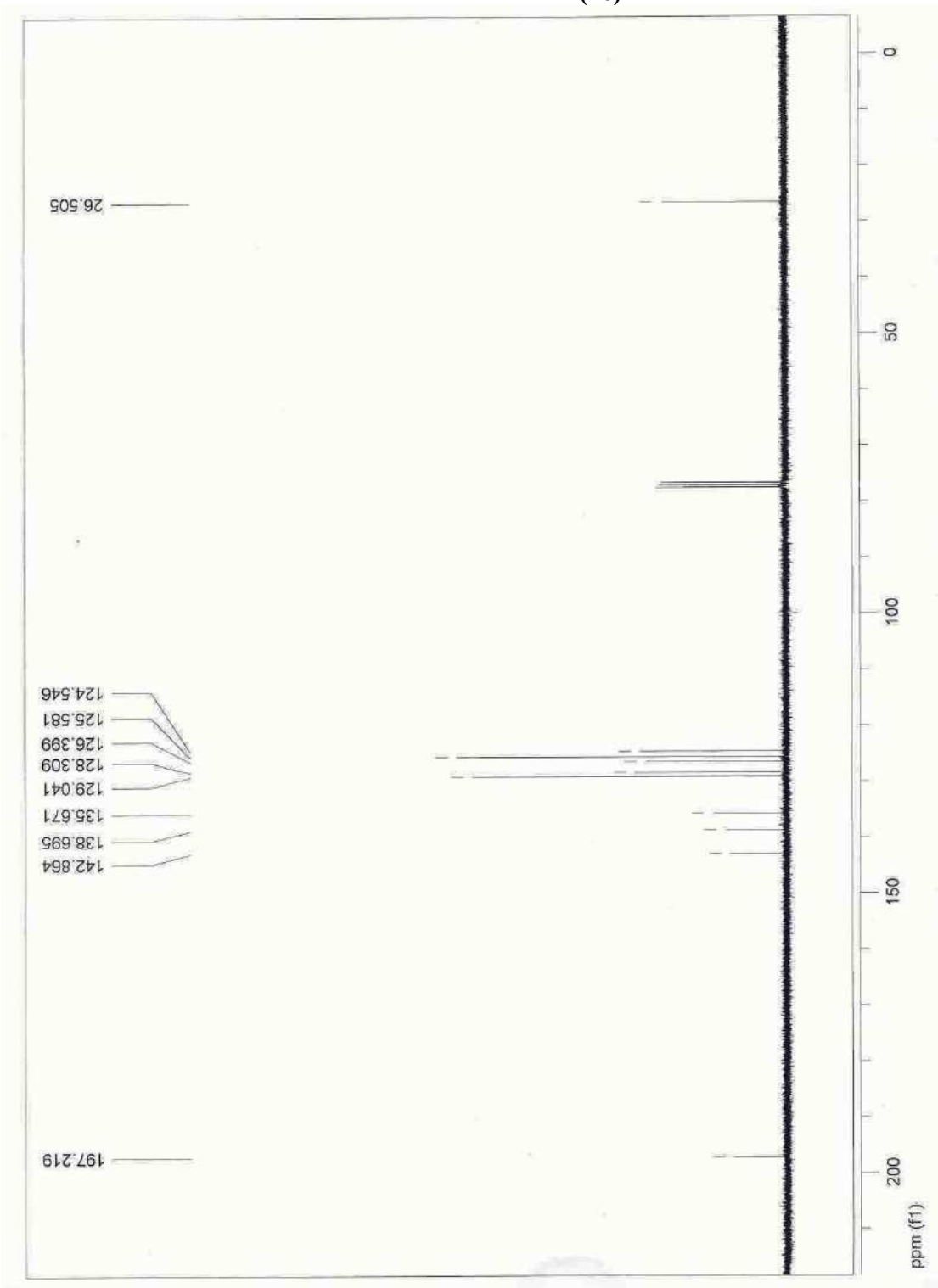
S

(2c)


26.505
124.546
125.581
126.399
128.309
129.041
135.671
138.695
142.864
197.219
0
50
100
150
200
ppm (f1)